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(54) ELASTICISED PLASTICS

(71) We, BAYER AKTIENGESELLSCHAFT, body corporate organised under the laws of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to elasticised plastics. In particular, the invention relates to mixtures hardenable by polyamines of epoxide compounds and polyaddition compounds containing carbamic acid phenyl ester groups, and to a process for producing epoxy/urea resins from mixtures of this kind.

Epoxide resins, especially those obtained from diphenylol propane and epichlorohydrin, are known starting materials for the production of cast resins and coatings. The epoxide resins hardened with polyamides are hard and resistant to chemicals but they frequently have the disadvantage that they lack elasticity.

This disadvantage applies in particular to the aromatic epoxide resins derived from diphenylol propane (bisphenol A) and epichlorohydrin. However, these very resins are distinguished by various desirable properties. As well as outstanding resistance to chemicals and solvents, the aromatic epoxide resins hardened with polyamides show outstanding bond strength on various substrates. The extreme hardness of amine-hardened epoxide resins is frequently undesirable in practice. A degree of flexibility and hence better impact strength are often desirable. The coating of concrete structures requires, for example, elastic coatings which are able to cover shrinkage-induced cracks in the concrete.

In practice, the elasticity of epoxide resins can be controlled to a certain extent by using suitable hardening agents. Conventional polyamines, for example ethylene diamine or di-

ethylene triamine can be converted into poly-aminoamides by reaction with polybasic acids prepared from fatty acids. In addition, hardening agents can be produced from chloroparaffins and ethylene diamine. Amine donors, for example ketimines, are also known which hydrolyse in conjunction with atmospheric moisture and liberate the amine required for hardening the epoxide resins.

Another method of producing elastic epoxide resins is to use aliphatic polyalcohols for the synthesis of the polyepoxides. Unfortunately, these polyepoxides show some serious disadvantages, for example, their resistance to chemicals is poor in comparison with polyepoxides produced from aromatic polyphenols.

Conventional methods of external plasticisation can only be applied to a limited extent to epoxide resins. Apart from the poor compatibility of amine-hardened epoxide resins with conventional plasticisers, which is reflected in exudation of the plasticiser from the hardened resin, elasticity is barely improved by the addition of plasticisers whilst structural strength is, in fact, significantly impaired.

It is also known from German Patent Specification No. 1,086,372 that coating agents hardening at room temperature or elevated temperature can be produced from mixtures of carboxylic acid amidoamines, especially amidoamines of dimerised and trimerised fatty acids, and isocyanate-group-free polyurethanes of tolylene diisocyanates and monophenols or the reaction product of 1 mol of trimethylol propane, 3 mols of tolylene diisocyanate and 3 mols of phenol, dissolved in suitable solvents. It is pointed out that simple polyamines instead of the basic amidoamines give rise to inadequate adhesion of the coatings. According to a Patent of Addition to the above-

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- mentioned Patent, namely German Patent Specification No. 1,090,803, addition of small quantities of epoxide resin to the mixture of polyurethane and amidoamine results in an improved bond strength. As can be seen from German Patent Specification No. 1,160,176, however, mixtures of this kind are not stable in storage. They have inadequate pot lives and gelatinise after a short time.
- The present invention provides hardenable plastics mixtures of epoxide compounds, compounds containing amino groups and products containing carbamic acid aryl ester groups, characterised by
- a) a synthetic resin component having free epoxide groups corresponding to an "epoxy value" as hereinafter defined in the range of from 0.02 to 0.6 and a molecular weight of from 300 to 7000;
 - b) a synthetic resin component having carbamic acid aryl ester groups of a polyalkylene ether polyol, polyalkylene thioether polyol, polyacetal, polyesteramide or polyester polyol and a diisocyanate or polyisocyanate and an optionally substituted phenol; and
 - c) a polyamine compound having at least two active hydrogen atoms attached to the nitrogen of the amino groups or active hydrogen atoms which are thermally liberated.
- By the term "epoxy value" we mean the number of epoxide equivalents in 100 g of resin.
- The invention also provides a process for producing a shaped article or sheet structure, wherein
- a) a synthetic resin compound having free epoxide groups corresponding to an epoxy value in the range of from 0.02 to 0.6 and a molecular weight of from 300 to 7000;
 - b) a synthetic resin component containing carbamic acid aryl ester groups or a polyalkylene ether polyol, polyalkylene thioether polyol, polyacetal, polyesteramide or polyester polyol and a diisocyanate or polyisocyanate and an optionally substituted phenol; and
 - c) a polyamine compound having at least two active hydrogen atoms attached to the nitrogen of the amino groups, which may be thermally liberated, or active hydrogen atoms, are mixed and hardened while forming either at room temperature or at elevated temperature.
- The compounds containing carbamic acid aryl ester groups which are used in the process according to the invention can be linear or branched. They have an average molecular weight of from 500 to 10,000 and can be obtained by conventional methods. These compounds are preferably obtained by reacting corresponding polymerisation or polycondensation products containing isocyanate groups with phenol or phenol derivatives, preferably in stoichiometric quantities, optionally at elevated temperatures in the presence of the usual catalysts such as tertiary amines and/or tin compounds. The polymerisation or polycondensation products containing isocyanate groups (isocyanate pre-polymers), can, in turn, be obtained by reacting the corresponding polymerisation or polycondensation products containing hydroxyl, amine or sulphhydryl groups, preferably the conventional hydroxyl-group containing polyethers, polythioethers, polyesters, polyacetals or polyesteramides, with diisocyanates or polyisocyanates, for example in an NCO:OH ratio of from 1.5 to 2.5, or with a large excess of isocyanate, and subsequently removing the excess isocyanate, for example by thin-layer distillation.
- According to a particular embodiment of the invention, the compound containing carbamic acid aryl ester groups is a polyaddition compound of tolylene diisocyanate, propylene glycol ether and alkyl phenol.
- Preferred linear and branched polymerisation or polycondensation products containing hydroxyl, sulphhydryl groups or primary or secondary amino groups, include those with hydroxyl groups which have an average molecular weight of from 150 to 10,000.
- The following are mentioned by way of example: polyalkylene ether polyols obtained by the anionic polymerisation, copolymerisation and block copolymerisation of alkylene oxides, such as ethylene oxide, propylene oxide and butylene oxide, with bifunctional or polyfunctional alcohols such as 1,4-butane diol, 1,1,1-trimethylol ethane, 1,1,1-trimethylol propane, 1,2,6-hexane triol, glycerin, pentaerythritol and sorbitol, or with amines such as methyl amine, ethylene diamine and 1,6-hexamethylene diamine, as starting components or by the cationic polymerisation and copolymerisation of cyclic ethers such as tetrahydrofuran ethylene oxide and propylene oxide, with acid catalysts such as boron trifluoride etherate, and by the polycondensation of glycols which eliminate water on polycondensation, such as 1,6-hexane diol, in the presence of acid etherification catalysts, such as *p*-toluene sulphonic acid, and, for example in order to obtain a fire-proof effect, oxalkylation products of phosphoric acid and phosphorous acids, for example with ethylene oxide, propylene oxide, butylene oxide and styrene oxide.
- Preferred polyalkylene thioether polyols include the polycondensation products of thiodiglycol with itself and with diols and/or polyols such as, for example, 1,6-hexane diol, triethylene glycol, 2,2-dimethyl-1,3-propane diol and 1,1,1-trimethylol propane, in the presence of acid etherification catalysts such as phosphoric acid and phosphorous acid.
- Preferred polyacetals include the polycondensation products of formaldehyde and diols and/or polyols, such as diethylene glycol,

triethylene glycol, 1,4-butane diol, 1,6-hexane diol, thiodiglycol and 1,1,1-trimethylol propane, with acid catalysts such as phosphoric acid and *p*-toluene sulphonic acid.

5 Preferred polyester polyols include the condensation products of di- and/or polycarboxylic acids and diols and/or polyols of the kind obtained by polycondensing, for example, adipic acid, phthalic acid, tetra-
10 hydrophthalic acid, hexahydrophthalic acid and endomethylene tetrahydrophthalic acid with ethylene glycol, 1,4-butane diol, diethylene glycol, triethylene glycol, 1,6-hexane diol, 2,2-dimethylol-1,3-propane diol, 1,1,1-trimethylol propane and 1,2,6-hexane triol,
15 also polycarbonates of the aforementioned diols and polyols and polyamides obtained through the additional presence of amino alcohols such as ethanolamine for example,
20 and polymerisation products of lactones such as ϵ -caprolactone.

The aforementioned polymerisation and polycondensation products together with diisocyanates and/or polyisocyanates are converted by conventional techniques into isocyanate prepolymers containing isocyanate groups. If a further chain-extending reaction through urethane groups is desired the polymerisation or polycondensation products
25 which contain hydroxyl groups are reacted while cooling with the diisocyanates or polyisocyanates initially at a temperature of from 0 to 25°C and the, optionally after heating for several hours, preferably at a temperature
30 of from 50 to 120°C with an NCO:OH ratio of from 1.5 to 2.5 and preferably with an NCO:OH ratio of from 1.8 to 2.2. If a chain-extending reaction is not required, a considerably larger excess of the diisocyanate or polyisocyanate, preferably calculated for an NCO:OH ratio of from 3 to 5, is used
40 although in other respects the procedure is the same as for the lower NCO:OH ratios. In this case, the excess diisocyanate or polyisocyanate is ultimately removed by thin-layer distillation, for example in the case of distillable diisocyanates or polyisocyanates, or by solvent extraction in the case of non-distillable isocyanates.

50 The following are examples of suitable diisocyanates or polyisocyanates: tolylene-2,4-diisocyanate and its commercial-grade mixtures with tolylene-2,6-diisocyanate, tolylene-2,6-diisocyanate, diphenyl methane-4,4'-diisocyanate, 1,6-hexamethylene diisocyanate, naphthylene-1,5-diisocyanate, *m*-xylylene diisocyanate, 1-methyl-2,4-diisocyanato cyclohexane, isophorone diisocyanate, 2,4,4-trimethyl-1,6-diisocyanato hexane,
55 dimeric tolylene-2,4-diisocyanate, N,N'-di-(4-methyl-3-isocyanato phenyl)-urea, N,N',N''-tri-(6-isocyanatohexyl)biuret, triphenylmethane-4,4',4''-triisocyanate, the reaction product of 3 mols of tolylene-2,4-diisocyanato
60 and 1 mol of 1,1,1-trimethylol propane, tri-

merisation and polymerisation products of tolylene-2,4-diisocyanate, mixed-trimerisation and mixed-polymerisation products of tolylene-2,4-diisocyanate and 1,6-hexamethylene diisocyanate, mixtures of isomeric
70 diphenyl methane diisocyanates, polyisocyanates containing more than two benzene nuclei each attached through methane groups and diisocyanates of diphenyl methane structure some of whose isocyanate groups are converted into carbodiimide groups.

The polymerisation or polycondensation products containing isocyanate groups obtained from the aforementioned components by known methods are subsequently converted into carbamic acid phenyl esters by known reaction with phenols, preferably in stoichiometric quantities. This reaction is advantageously carried out at elevated temperatures, preferably at temperatures of from 50 to 120°C, and optionally in the presence of the catalysts commonly used in isocyanate chemistry, for example tertiary amines and/or compounds of divalent and tetravalent tin.

90 The polymerisation and polycondensation products which contain isocyanate groups can be prepared either in bulk or in solvents which are inert to isocyanates. On completion of the reaction, any solvents used are removed by distillation, preferably by thin-layer distillation. However, it is of advantage in some cases further to use the solutions of the isocyanate prepolymers as such.

Examples of suitable solvents include esters such as ethyl acetate, butyl acetate, methylglycol acetate and ethylglycol acetate, ketones such as methylethyl ketone, methyl-isobutyl ketone, aromatic solvents such as toluene, xylene and mixtures of higher aromatic solvents, also mixtures of the aforementioned solvents.

The chain-extending agents which contain hydroxyl groups, and which are commonly used for reactions carried out by the isocyanate-polyaddition technique may optionally be used to prepare the bifunctional and polyfunctional polymerisation or polycondensation products which contain isocyanate groups. In addition to a chain-extending reaction, it is possible, for instance by using a polyfunctional chain-extending agent, to produce bifunctional polymerisation and polycondensation products which are branched only through urethane groups. The viscosity of the isocyanate prepolymers can optionally be reduced to the required level by the increased content of the urethane groups where chain-extending agents are used.

115 Preferred chain-extending agents for this purpose include compounds which contain hydroxyl groups such as, 1,4-butane diol, 1,1,1-trimethylol propane and hydroquinone-di-(2-hydroxy-ethyl ester).

Suitable catalysts which can be used in quantities of from 0.001 to 2%, include for
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example diazabicyclooctane, dibutyl tin dilaurate and tin (II)-octoate.

In addition to phenol itself, a large number of substituted phenols are suitable for use in the preparation of the carbamic acid aryl esters employed in accordance with the invention. The following are mentioned in particular: *o*-, *m*- and *p*-cresol, cresol mixtures, the isomeric xylenols, 2-sec-butyl phenol, 4-tert-butyl phenol, 4-(1,1,3,3-tetramethyl butyl)-phenol, 4-cyclohexyl phenol, 4-nonyl phenol mixtures containing branched nonyl radicals, dodecyl phenol mixtures of the kind which can be obtained, for example, by the chemical addition of suitable olefins to phenols in the presence of Friedel-Crafts catalysts, also amyl-, hexyl-, heptyl-phenol, 4-nitrophenol, 4-chlorophenol pentachlorophenol, α - and β -naphthol and 4-hydroxy benzoic acid methyl ester, 4-hydroxy benzoic acid-*n*-butyl ester and 4-hydroxy benzoic acid (2-ethyl hexyl ester).

Phenol and low-alkyl-substituted (C_1-C_4) phenols are generally evolved from the end-products. This may possibly give rise to the release of noxious odours which is unacceptable on physiological grounds and also to undesirable mass shrinkage. For this reason, it is particularly preferred to use phenols of the kind substituted by C_1-C_4 -alkyl radicals in the preparation of the polymerisation or polycondensation products containing carbamic acid aryl ester groups used in accordance with the invention.

In addition to the preferred process for producing the carbamic acid aryl esters used in accordance with the invention which has been described in detail in the foregoing, it is of course also possible to use other methods of production known *per se*. Thus, the corresponding carbamic acid chloride can be obtained, for example, by reacting linear or branched polymerisation or polycondensation products containing primary or secondary amino groups with phosgene, giving carbamic acid esters when reacted in a second stage with sodium salts of phenols. Polymerisation or polycondensation products containing amino groups can also be converted into carbamic acid phenyl esters in a single stage with the chloroformic acid esters of the corresponding phenols in the presence of hydrogen chloride acceptors.

The polyepoxides which can be used in accordance with the invention are substances containing more than one epoxide group. They can be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic, optionally substituted for example by chlorine atoms, hydroxyl-, cyano- or ether groups. The glycidyl polyethers of diphenylol propane having an epoxy value of from 0.02 to 0.6 and a molecular weight of from 340 to 7000 are particularly preferred. Active diluents, for example, styrene oxide, butyl

glycidyl ether, glycidyl esters of synthetic, highly branched predominantly tertiary aliphatic monocarboxylic acids, or cycloaliphatic mono epoxides such as 3-vinyl-2,4-dioxaspiro-(5,5)-9,10-epoxy undecane, may optionally be added to the polyepoxides to lower their viscosity.

According to this invention, polyamines or amine donors are used in conjunction with the polyepoxides. In the context of the invention, compounds of this kind are the compounds containing amino groups which are normally used to harden polyepoxides, for example aliphatic, cycloaliphatic or heterocyclic polyamines or polyamidoamines. Preferred aliphatic polyamines are alkylene polyamines corresponding to the formula:



in which R represents a divalent hydrocarbon radical having from 2 to 18 carbon atoms whilst *n* is an integer of from 1 to 6.

The following are examples of suitable polyamines: ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 1,4-aminobutane, 1,3-diaminobutane, hexamethylenediamine, 3-(*n*-isopropyl amino)-propylamine, *N,N'*-diethyl-1,3-propanediamine, hexapropyleneheptamine, penta-(1-methyl propylene)-hexamine, tetrabutylene-pentamine, hexa-(1,1-dimethyl ethylene)-heptamine, di-(1-methyl butylene)- triamine, pentamylhexamine, tri - (1,2,2 - trimethyl ethylene)-tetramine, tetra-(1,2 - dimethyl propylene)-pentamine, penta-(1,5-dimethyl amylene)-hexamine, penta-(1,2-dimethyl-1-isopropyl ethylene)-hexamine and *N,N'*-dibutyl-1-6-hexanediamine.

Further examples of polyamines are those with 1 or more cycloaliphatic rings such as 1-cyclohexylamino-3-amino propane, 1,4-diaminocyclohexane, 1,3-diaminocyclopentene, di-(aminocyclohexyl)-methane, di-(aminocyclohexyl)-sulphone, 1,3-di-(aminocyclohexyl)-propane, 4-isopropyl-1,2-diaminocyclohexane, 2,4-diaminocyclohexane, *N,N'*-diethyl-1,4-diaminocyclohexane, isophorone diamine and 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane. Diprimary cycloaliphatic amines are particularly suitable for the mixtures according to the invention.

Suitable heterocyclic polyamines include, for example, *N*-(amino alkyl)-piperazines such as *N*-aminobutylpiperazine, *N*-(amino isopropyl)-3-butoxypiperazine, *N*-aminoethylpiperazine, 2,5-dibutyl-*N*-aminoethylpiperazine, 2,5-dibutyl-*N*-aminoethylpiperazine with alkyl groups preferably having no more than 6 carbon atoms whilst the entire molecule contains no more than 18 carbon atoms.

Other hardeners containing several amino hydrogen atoms include polyamides of an aliphatic or cycloaliphatic polycarboxylic acid with an aliphatic amine. The resulting pro-

duct contains groups which are reactive with epoxy groups, such as amino groups or carboxyl groups.

5 Examples of polybasic acids suitable for producing these polyaminoamides include dimerised and trimerised unsaturated fatty acids produced from the polymerisation of fatty acids by thermally drying oils. In some cases, it is advantageous to use two or more
10 of the aforementioned polyamines in admixture with another.

Suitable amine donors include the condensation products of the described polyamines with aliphatic, cycloaliphatic, araliphatic and aromatic ketones. They are best prepared, for example, by continuously removing the water formed during condensation from the reaction mixture by azeotropic distillation. The amine donors are particularly valuable for the production of one-component systems which are hardened by the hydrolysing effect of atmospheric moisture.

The mixtures according to the invention contain between 5 and 9% of compounds containing carbamic acid aryl ester groups, based on the polyepoxide compound used. The quantities in which the polyamine is used are generally selected in accordance with the stoichiometric ratios. However, an excess
30 of up to 50%, based on the stoichiometric quantity, is still acceptable. The compounds containing carbamic acid aryl esters are preferably added to the epoxide resin compound before the hardener is added.

35 Fillers, pigments, solvents, plasticisers, thickeners, and, in the case of one-compound systems, drying agents can also be added to prepare the final mixture in the form in which it is ready for use. It is also possible to introduce substances which extend the mixtures or which are intended to act as adhesion promoters, such as tar and tar pitch, asphalt, and other plastics such as phenol-, aldehyde-, phenol-urea plastics,
45 vinyl plastics, polyolefins and synthetic rubbers.

Suitable fillers include sand, crushed rock, calcium sulphate, calcium carbonate, aluminium powder, also silica, asbestos powder, kaolin and talcum.

50 Examples of suitable solvents, which especially to adjust the required viscosity, may be used in quantities of from 5 to 75%, but preferably in quantities of less than 24% by weight, based on the mixture as a whole,
55 include aromatic solvents such as toluene, xylene, alcohols such as methanol and isopropanol, esters such as ethylacetate and ethylglycol acetate, ketones such as acetone and methylisobutyl ketone. The aforementioned drying agents can include molecular-sieve zeolites such as sodium aluminosilicate, orthoformic acid esters, low-molecular weight isocyanate compounds such as phenyl iso-

65 cyanate, also metal alcohols such as aluminium isobutylate and titanium tetrabutylate.

Catalysts which accelerate hardening can also be used. Catalysts such as these include the accelerators normally used in epoxide resin chemistry such as, for example, the reaction products of phenol or substituted phenols with formaldehyde and ammonia. These accelerators are added in quantities of from 0.5 to 5%, based on the hardenable plastics mixture.

The mixtures according to the invention are suitable for castings and cast resins which are required to be particularly elastic. It is possible to produce one-component and two-component systems which are suitable, for example, for roof coatings and floor coatings.

Coatings prepared with the mixtures according to the invention can also be used for protecting metals against wear. Hardening is accelerated by applying elevated temperatures. Textile fabrics or glass mats can be introduced. The end products can be used in the form of putty-like compositions as sealing compounds in the building industry. It is remarkable that the problem of inadequate inter-layer adhesion does not occur with the mixtures according to the invention. This effect is particularly acute in the case of pure epoxide resins in cases where, in multiple-layer film coating, there are long periods of waiting between individual coating operations. Pure epoxide resin films show inadequate bond strength under these conditions whilst the mixtures according to the invention show outstanding inter-layer adhesion, even after prolonged ageing.

The invention is illustrated by the following Examples.

Preparation of the starting materials:

A. Preparation of a trifunctional polyether with terminal carbamic acid-(4-nonylphenyl ester)-groups: 105

1000 g of a trifunctional polypropylene glycol with an OH number of 56, obtained in conventional manner by the anionic polymerisation of propylene oxide with 1,1,1-trimethylol propane or its sodium alcoholate as starting material, and 150 g of tolylene-2,4-diisocyanate were mixed at 20 to 25°C. This mixture was heated to 70°C for 5 hours with stirring, after which it had an NCO-content of 3% by weight. 5 g of dibutyl tin dilaurate and 190 g of a commercial-grade 4-nonylphenol mixture containing branched nonyl radicals, were added to the isocyanate prepolymer cooled to 20—25° C. This was followed by heating to 70°C for another 4 hours with stirring. Thereafter, the material contained hardly any isocyanate and had an equivalent weight of approximately 16300.

B. Preparation of a trifunctional polyether

with terminal carbamic acid phenyl ester groups:

- 5 The procedure was as in A above, except that the isocyanate prepolymer obtained from the trifunctional polyether and tolylene-2,4-diisocyanate was reacted for 4 hours at 70°C with 81 g of phenol instead of with 190 g of the commercial-grade 4-nonyl phenol mixture in the presence of 5 g of dibutyl tin dilaurate. The reaction material had an equivalent weight of approximately 1500 and contained hardly any more isocyanate.

Example 1

800 Parts of weight of the carbamic acid

30	Breaking strength	DIN 53 504	45 kp/cm ²
	Breaking elongation	DIN 53 504	145 kp/cm ²
	Tear propagation resistance	DIN 53 515	23 kp/cm ²
	Shore hardness A		75
	Volume resistance	DIN 53 482	3.0.10 ¹⁴ ohms. cm
	Dielectric strength	DIN 53 481	274 kv/cm

Example 2

Preparation of an elasticised epoxide resin coating composition:

- 1000 Parts by weight of a mixture of 700 parts by weight of a liquid, bifunctional epoxide resin of epichlorohydrin and bisphenol A with an epoxide equivalent weight of 185 and 300 parts by weight of phenyl glycidyl ether were mixed with 1000 parts by weight of the carbamic acid phenyl ester produced in accordance with B. 100 Parts by weight of benzyl alcohol and 500 parts by weight of isopropanol were added to this mixture, and 1400 parts by weight of barium sulphate, 180 parts by weight of titanium dioxide and 20 parts by weight of pigment black were introduced by means of a three-roll mill.

- Before the coating composition was processed, a mixture of 360 parts by weight of 3,3'-dimethyl-4,4'-diamino dicyclohexyl methane and 80 parts by weight of a Mannich base of 2 mols of phenol, 4 mols of ammonia and 5 mols of formaldehyde, was added as hardening component. The last of these compounds acts as a hardening accelerator.

- After the base component had been mixed with the hardening component, the coating

aryl ester compound A just described were mixed with 200 parts by weight of a liquid epoxide resin of bisphenol A and epichlorohydrin with an epoxide equivalent weight of 185. 50 parts by weight of phenoxy propanol were added to the resulting mixture as diluent. Before use, 110 parts by weight of 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane were stirred in as hardener. This mixture had a processing life of approximately 3 hours. It could be used as an embedding composition for electrical components and for general protection against corrosion. The hardened resin had the following properties:

composition was applied to concrete by means of a roller. The composition adhered even to damp concrete. It hardened overnight to form a coating of outstanding impact strength. Bond-strength testing showed that the bond strength of the coating was greater than the tensile strength of concrete (greater than 60 kg/cm²).

Comparison tests:

1000 Parts by weight of a conventional epoxide resin of diphenylol propane and epichlorohydrin with an epoxide equivalent weight of 190 are mixed with 126 parts by weight of diethylenetriamine and the resulting mixture was cast in moulds (test 1). For comparison, 600 parts by weight of the same epoxide resin were mixed with 400 parts by weight of dibutyl phthalate and hardened with 7.6 parts by weight of diethylene triamine (test 2). In a third test, a mixture of 600 parts by weight of the epoxide resin and 400 parts by weight of the carbamic acid aryl ester compound of A) was reacted with 10.5 parts by weight of diethylene triamine (test 3 according to the invention).

The mechanical properties were determined on standard test specimens (DIN 53 455):

90		Test 1	Test 2	Test 3
	Shore hardness D	84	76	65
	E-modulus kp-cm ²	32 400	15000	5 660
	Breaking elongation %	4.9	9.4	39.0

- 95 The superiority of the process according to the invention compared to "external" plasticisers such as dibutyl phthalate was reflected in test 3 in the high breaking elongation value and the low modulus of elasticity.

WHAT WE CLAIM IS:—

1. A hardenable plastics mixture comprising:
a) a synthetic resin component having free epoxide groups corresponding to an "epoxy

- value" as herein defined in the range of from 0.02 to 0.6 and a molecular weight of from 300 to 7000;
- 5 b) a synthetic resin component having carbamic acid aryl ester groups of a polyalkylene ether polyol, polyalkylene thioether polyol, polyacetate, polyesteramide or polyester polyol and a diisocyanate or polyisocyanate and an optionally substituted phenol; and
- 10 c) a polyamine compound having at least two active hydrogen atoms attached to the nitrogen of the amino groups or active amino hydrogen atoms which may be thermally liberated.
- 15 2. A hardenable synthetic resin mixture as claimed in claim 1, wherein the component having free epoxide groups is a condensation product of bisphenol A and epichlorohydrin.
- 20 3. A hardenable synthetic resin mixture as claimed in claim 1 or 2, wherein the component containing carbamic acid aryl ester groups is a polyaddition compound of tolyene diisocyanate, propylene glycol ether an alkyl phenol.
- 25 4. A hardenable synthetic resin mixture as claimed in any of claims 1 to 3, wherein the polyamine compound is a diprimary cycloaliphatic amine.
- 30 5. A process for producing a shaped article or sheet structure, wherein
- a) a synthetic resin component having free epoxide groups corresponding to an "epoxy value" as herein defined in the range of from 0.02 to 0.6 and a molecular weight of from 300 to 7000;
- b) a synthetic resin component containing carbamic acid aryl ester groups of a polyalkylene ether polyol, polyalkylene thioether polyol, polyacetal, polyesteramide or polyester polyol and a diisocyanate or polyisocyanate and an optionally substituted phenol; and
- c) a polyamine compound having at least two active hydrogen atoms attached to the nitrogen of the amino groups, which may be thermally liberated, or active hydrogen atoms, are mixed and hardened while forming either at room temperature or at elevated temperature.
6. A hardenable plastics mixture as claimed in claim 1 substantially as herein described with reference to any one of the specific Examples.
7. A process as claimed in claim 5, substantially as herein described with reference to any of the specific Examples.
8. A shaped article or sheet structure produced by process of claim 5 or 7.

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